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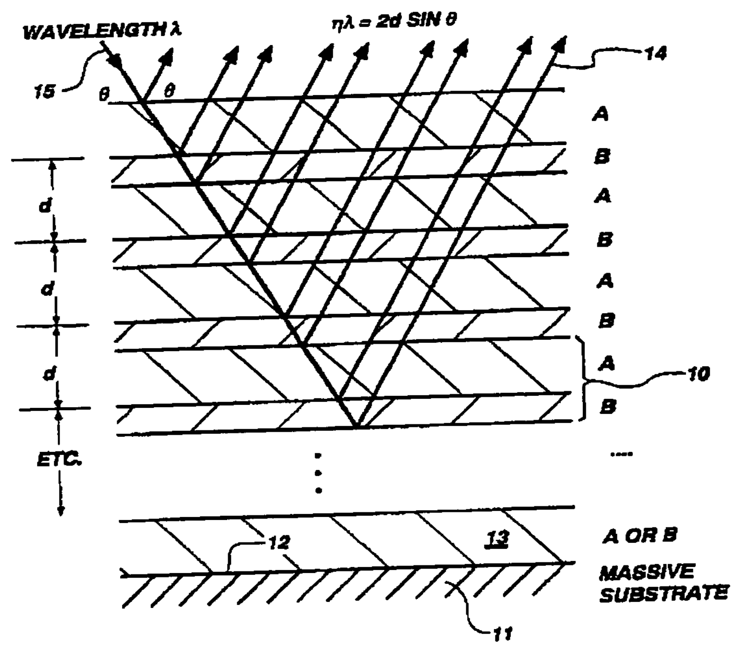
(54) Title: DEVICE AND METHOD FOR REFLECTION AND DISPERSION OF X-RAYS



(57) Abstract

A device and method for reflecting X-ray radiation having a wavelength within the approximate range of 5 to 32 angstroms. The device includes a substrate (11) with alternating layers (A and B) of nonmetallic tungsten carbide composition and boron carbide. The method includes preparation of such a multilayered device with sputtering techniques which include an environment of methane or other hydrocarbon to develop a hydrogenated component. The resultant multilayered reflective device provides improved reflectivity, more defined layer interface properties and reduced background for use in elemental X-ray spectroscopy.

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DEVICE AND METHOD FOR REFLECTION AND DISPERSION OF X-RAYS

BACKGROUND

1. Field of the Invention

This invention relates to soft x-ray optics and methods for reflection and dispersion of x-rays having wavelengths within the range of 5 to 32 angstroms. More particularly, it relates to preparation of x-ray mirrors and dispersion elements operable within this range of wavelengths in x-ray spectrometers and imaging and non-imaging systems.

2. Prior Art

The use of x-rays as an analytical tool is currently being applied in many fields of technology. X-ray spectroscopy, for example, enables elemental analysis by irradiation of a sample with high energy electrons, protons or photons to excite atoms which then emit characteristic x-rays whose wavelength values depend on atomic structure of the excited atom. Each element has a unique emission pattern which can be identified if the emitted radiation can be accurately detected. Obviously, such detection depends upon one's ability to differentiate differing wavelengths forming the emission. Typically, this is accomplished by processing the radiation through a system of reflection or dispersion elements for subsequent detection.

Other applications of x-ray analysis arise because x-rays exhibit properties similar to those of light waves generally. Accordingly, x-ray optics have been

applied to develop imaging applications in astronomy, biology, medical research, microlithography, and research in thermonuclear fusion, synchrotron radiation and related fields. Numerous devices have been developed for implementing such applications and generally are only as accurate as the optical elements that reflect, refract or diffract the radiation.

Multilayer x-ray optics, as developed by Spiller and Barbee, can be manufactured with multiple-layered structures having a very small period (10 to 200 angstroms). The period consists of one layer of material having a low refractive index and a second layer in integral contact with the first layer, having a higher refractive index. These layers are stacked in multiples to develop an effective reflectivity device which operates according to Bragg's law $n\lambda = 2d \sin \theta$.

The technology to make these structures usually involves sputtering or vapor deposition of the desired composition onto a substrate in the form of a thin layer. As used herein, thin layer means a layer which is sufficiently thin to be optically responsive to incident x-ray radiation by causing reflection, refraction or diffraction. Typical layer thickness for x-rays with wavelengths within the range of 5 to 32 angstroms will be from several angstroms to approximately 100 angstroms. Such thin layers may also be formed by molecular beam epitaxy, atomic layer growth

and other methods of thin film deposition known within the art.

The response of these multilayered, thin films to radiation is primarily affected by optical constants numerically represented by index of refraction and index of absorption values. The value of these optical constants within materials exposed to radiation within the soft x-ray region is determined by the electron density of the solid films and by electronic transition energy levels within the atoms. As a general rule, the heavy elements have relatively high indices of refraction and absorption, and the light elements have relatively low indices of refraction and absorption.

In order to obtain high reflection from a multilayered optical device, the alternating layers are selected to maximize the difference in the index of refraction between materials comprising the respective layers while minimizing the absorption. In other words, a material having a low index of refraction is chosen as the composition for one layer and a composition with a high index of refraction is selected for the second layer. The multilayered configuration therefore provides an alternating sequence of materials whose respective indices of refraction are alternately high and low, generating a high degree of reflectivity.

It is well known to use pure heavy metals or mixtures of heavy metals as the thin layer representing a high index of refraction. One such well known

material is elemental tungsten or tungsten alloy. The contrasting low index materials are represented by carbon, silicon, boron and other similar compositions. Combinations of these materials have been used to provide a multilayered optics device; however, the response of such devices has not been optimized, except by implementation of very expensive processes which focus on the mechanics of generating smooth surfaces at the atomic scale. For example, current practice emphasizes use of single elements of metallic substance as the layer composition, with an expectation that materials formed of single elements are more likely to form a smoother surface layer with greater uniformity of layer thickness.

A second focus of current fabrication procedure focuses on mechanical procedures for generating an abrupt interface between the respective layers. Typically, this has been viewed as a manufacturing problem. Specifically, it is recognized that high reflectivities which may be predicted by the difference in optical constants are not usually realized in the actual manufactured optical device. In fact, significant losses in reflectivity arise because diffusion and chemical reaction between the respective layers prevent formation of an abrupt boundary condition. This is particularly true within thin films as defined in this disclosure because the atomic diameters are significant compared to the thickness of

each layer. Consequently, any diffusion of material between layers or chemical reaction can result in a roughened interface.

OBJECTS AND SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a device and method for enhanced reflectivity of a multilayered optics device operable within the soft x-ray region.

It is a further object of this invention to provide a multilayered reflective device which offers enhanced reflectivity yet improved economy in manufacture.

Yet another object of this invention is to provide an optical device for use with x-rays within the wavelength range of 5 to 32 angstroms, which greatly reduces the loss of reflectivity due to diffusion and chemical reaction between the layers of material.

These and other objects are realized in a method for preparing a reflective device for x-ray radiation having a wavelength generally within the range of 5 to 32 Angstroms. This method comprising the steps of selecting a substrate having a smooth surface suitable for supporting a reflective coating operable within the x-ray wavelength range of 5 to 32 Angstroms; and applying over the substrate a thin layer of nonmetallic composition comprised substantially of tungsten carbide as an interstitial compound or as a stoichiometric composition, possibly including some hydrogen. A thin layer of composition comprised substantially of boron

carbide or an equivalent low index material is then applied to the first layer, providing an abrupt interface between the respective layers. Additional layers may be added in like manner to increase the effectiveness of the device.

Other objects and features of the present invention will be apparent to those skilled in the art, in view of the following detailed description, taken in combination with the accompanying drawings wherein:

Figure 1 depicts a graphic cross-section of a multilayer reflector including a substrate and alternating thin layers of material having high and low refractive indexes respectively.

Figure 2 shows a graph illustrating the theoretical reflectivities of WC/B_4C and W/Si over the wavelength range of 0 to 35 angstroms, using Vinogradov's approximation methods.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 shows a graphic cross section of alternating layers of material represented by "A" and "B". Two of such layers comprise a period 10 which has a thickness represented by the distance "d". These multiple layers are positioned over a substrate 11, which may be silicon or composition of other smooth surface whose physical characteristics are suitable for supporting a reflective coating operable within the x-ray wavelength range of 5 to 32 angstroms. This substrate is illustrated as a planar surface 12;

however, it will be known to those skilled in the art that curved surfaces and contours can likewise be utilized, provided the surface characteristics are suitable for reflection.

This construction begins with a first layer of A or B identified as item 13. Additional layers are deposited, one upon another, in alternating sequence as illustrated. It should be noted that the sequence can begin with either A or B, as long as the alternating order is maintained. The number of layers may be as small as 2, when used as a beam splitting system, or as many as 100 or more. The number of layers will be determined, in part, by the extent of reflectivity desired.

Superimposed over the multilayered matrix are reflected arrows 14 representing reflections of incident radiation 15. These reflections are dictated by the well known Bragg equation as shown at the top of figure 1.

The present inventors have discovered that the use of nonmetallic tungsten, such as tungsten carbide provides surprising enhancement to the reflectivity of such a multilayer reflective device as is illustrated in figure 1. As used herein, "tungsten carbide" includes both nonstoichiometric compounds wherein the tungsten and carbon are in interstitial configuration, as well as tungsten and carbon in stoichiometric relationships. It may also include some hydrogen. The effectiveness of

tungsten carbide is surprising for several reasons. First, prior art use of heavy metals has shown that metallic substances are effective, but does not suggest that nonmetallic compounds would provide an improved reflectivity over the metallic materials. For example, it is known that tungsten and tungsten alloys are appropriate composition for the high index refraction layer; however, it would not be anticipated that a refractory nonmetallic compound such as tungsten carbide would have equivalent or even better reflectivity characteristics as part of the multilayered optics device. This now appears to be the case.

It has also been discovered that some hydrogen atoms may be included within the tungsten carbide material without adversely affecting its performance. This observation is significant in view of the fact that the method of fabricating the tungsten carbide layer may involve the use of methane or other active hydrocarbons which may result in some hydrogenation within the nonmetallic tungsten carbide composition.

It has also been discovered that this composition of tungsten, carbon and hydrogen need not be in stoichiometric relationship, but in fact may be either stoichiometric or nonstoichiometric in composition. Accordingly, a representative formula for the thin layer comprised of tungsten carbide would be $W_x C_y H_z$ wherein x has a value greater than 0 and less than 3, y has a value greater than 0 and less than 4 and z has a value

within the range of 0 to 2y. Although the tungsten carbide composition alone appears to have general effectiveness in proving reflectivity, the use of tungsten, carbon, and perhaps hydrogen in these relative amounts appears to provide excellent response within the specific range of wavelengths from 5 to 32 angstroms.

The nonmetallic tungsten carbide composition is deposited on the substrate 11 by any method of deposition which will apply a uniform, thin layer. This layer may be as thin as several atomic diameters or may range up to 100 angstroms or more. The method disclosed in the preferred embodiment applies sputtering techniques which are well known in the industry. Specifically, DC magnitron sputtering guns are directed toward a tungsten target in the presence of a reactive hydrocarbon. The specific hydrocarbon used in the present case was methane. This gaseous environment also includes a noble gas, such as argon. Using this basic technique and a twelve percent methane concentration at a total pressure of 1.5 mtorr, multilayers including tungsten carbide compositions embodying some of the formulations set forth above for tungsten, carbon and hydrogen have been produced. Tests of these multilayers have been shown to have higher reflectivity than has previously been reported for use with just tungsten or tungsten alloys without the nonmetallic character of tungsten carbide. This has been confirmed particularly

in connection with magnesium and sodium kα x-ray emissions.

These tests were run using a low index or refraction layer comprised of boron carbide in combination with the above identified tungsten carbide. This boron composition was fabricated in a similar manner utilizing sputtering techniques wherein the target of B_4C was used. The formula for the composition of the boron carbide layer is $B_dC_eH_f$. Specific values for these subscripts are "d" values greater than 0 but less than 4, "e" values greater than 0 but less than 3, and values within the range of 0 to 2e for the subscript f. The presence of hydrogenated materials in this layer can reduce the density of the boron carbide, further enhancing reflectivity over that of stoichiometric B_4 C. Assuming the embodiment of figure 1 starts with layer A being that of tungsten carbide, layer B would comprise boron carbide, with alternating layers following sequentially.

The reflective device manufactured in accordance with the procedure outlined above was compared with a prior art tungsten/silicon multilayer system and showed surprising improvement. For example, figure 2 shows the theoretical reflectivities of tungsten carbide with boron carbide 20 and tungsten with silicon 21 as the respective layers of the multilayer configuration. The graph of figure 2 shows these theoretical reflectivities over the wavelength of 0 to 35 angstroms. These were

calculated using Vinogradov's approximation and optimized for layer thickness in the ratio between the high index layer and the bilayer period at each data point. The curve shows that the two material systems are very similar over this wavelength range, with high reflectivities for the tungsten carbide/boron carbide compositions for wavelengths shorter than the tungsten absorption edge at 6.6 angstroms, and slightly lower reflectivities for longer wavelengths. The difference between the two material systems, however, is insignificant because manufacturing defects account for much more variation than this. Therefore, based on theoretical comparisons, the tungsten carbide/boron carbide multilayered device should perform approximately equal to the W/Si device.

Nevertheless, measurements of actual reflectivity as compared to theoretical values demonstrated the combination of tungsten carbide with boron carbide to be more than twice as reflective as metallic tungsten with silicon. Specifically, whereas theoretical reflectivity of tungsten and silicon layers was 47.1% based on a composition identified for laboratory purposes as S366, actual reflectivity only measured 18%. In contrast, actual reflectivity for the tungsten carbide/boron carbide multilayered device was 44.1%, compared to the theoretical value of 51.2% Therefore, the process and device of the present invention yielded over 80% of the theoretical reflectivity, whereas the prior art

tungsten/silicon combination provided only 38% of the predicted reflectivity.

It is believed that part of the improvement experienced by the present invention arises from probably reaction of tungsten and silicon to form tungsten silicides which roughen and blur the interface, preventing the multilayer from achieving high performance. The use of tungsten carbide inhibits such reaction and preserves the desired abrupt interface between thin layers.

In addition to the enhanced reflectivity realized with the tungsten carbide composition, the use of boron carbide offers several benefits over the prior art use of silicon. Specifically, the presence of silicon in such multilayered devices is a disadvantage in x-ray fluorescence spectroscopy in certain applications, such as analysis of x-rays of the elements N, O, F, Ne, Na, Mg, Al, Si, P, and S. In analyzing materials containing a high percentage of calcium, the calcium kα radiation will excite the silicon in the multilayer, which will then emit silicon kα radiation. This will be detected directly by the x-ray detector, causing a high background against which low percentages of sodium and magnesium are difficult to measure. The present invention overcomes this deficiency by using the boron carbide layer within the device. This advantage has particular utility in the cement industry, where such

measurements are made in the presence of large percentages of calcium.

Although the preferred embodiments of this invention has been set forth, it is to be understood that this is by way of example, and is not to be considered limiting with respect to the claimed invention set forth hereafter.

CLAIMS

1. A method for preparing a reflective device for x-ray radiation having a wavelength approximately within the range of 5 to 32 Angstroms, said method comprising the following steps of a) plus the subsequent steps of b) and c) in any order:

a) selecting a substrate having a smooth surface suitable for supporting a reflective coating operable within the x-ray wavelength range of 5 to 32 Angstroms;

b) applying over the substrate a thin layer of nonmetallic composition comprised substantially of tungsten carbide;

c) applying to the previous layer of tungsten carbide a thin layer of composition optically compatible with the tungsten carbide and having a comparative low index of refraction therewith.

2. A method as defined in claim 1, further comprising the step of repeating steps b) and c) sequentially to form a multiple layered device.

3. A method as defined in claim 2, comprising the more specific step of applying at least one of the thin layers of composition by reactive ion sputtering techniques.

4. A method as defined in claim 3, comprising the more specific step of applying the nonmetallic tungsten carbide composition by reactive ion sputtering of a tungsten target in an atmosphere of noble gas and hydrocarbon.

5. A method as defined in claim 1, comprising the more specific step of applying boron carbide composition as the low index of refraction layer.

6. A method as defined in claim 5, comprising the more specific step of applying the boron carbide composition by reactive ion sputtering of a boron target in an atmosphere of noble gas and hydrocarbon.

7. A method as defined in claim 4 wherein the step of reactive ion sputtering is performed in an environment which includes methane as the hydrocarbon.

8. A method as defined in claim 6 wherein the step of reactive ion sputtering is performed in an environment which includes methane as the hydrocarbon.

9. A method as defined in claim 1, further comprising the steps of:

a) positioning the substrate with applied layers of tungsten carbide and boron carbide compositions within an x-ray wavelength dispersive spectrometer; and

b) processing a specimen within the spectrometer for detection of a predetermined element.

10. A method as defined in claim 9, comprising the more specific step of processing the specimen with the x-ray spectrometer for detecting an element selected from the group of elements consisting of nitrogen, oxygen, fluorine, neon, sodium, magnesium, aluminum, silicon, phosphorous and sulfur.

11. A device for reflecting and dispersing soft x-rays of wavelengths within the approximate range of 5 to 32 angstroms, comprising:

a substrate having a smooth surface suitable for supporting a reflective coating operable within the x-ray wavelength range of 5 to 32 Angstroms;

a plurality of alternating thin layers respectively including boron carbide and nonmetallic tungsten carbide in either order and being positioned on the substrate as a reflective coating, each layer having a thickness which causes reflection or dispersion of x-rays within the range of 5 to 32 angstroms which are incident upon the layers.

12. A device as defined in claim 11, wherein at least one of the layers including nonmetallic tungsten carbide also includes hydrogen.

13. A device as defined in claim 11, wherein at least one of the layers including boron carbide also includes hydrogen.

14. A device as defined in claim 11, wherein at least one of the layers including tungsten carbide is represented by the formula $W_xC_yH_z$ wherein W represents tungsten and alloys thereof, C represents carbon and H represents hydrogen, x having a value greater than 0 and less than 3, y having a value greater than 0 and less than 4, and z having a value within the range of 0 to 2y.

15. A device as defined in claim 11, wherein at least one of the layers including boron carbide is represented by the formula $B_dC_eH_f$ wherein B represents boron, C represents carbon and H represents hydrogen, d having a value greater than 0 but less than 4, e having a value greater than 0 but less than 3, and f having a value within the range of 0 to 2y.

16. A product formed by the method as defined in claim 1.

17. A product formed by the method as defined in claim 4.

18. A product formed by the method as defined in claim 5.

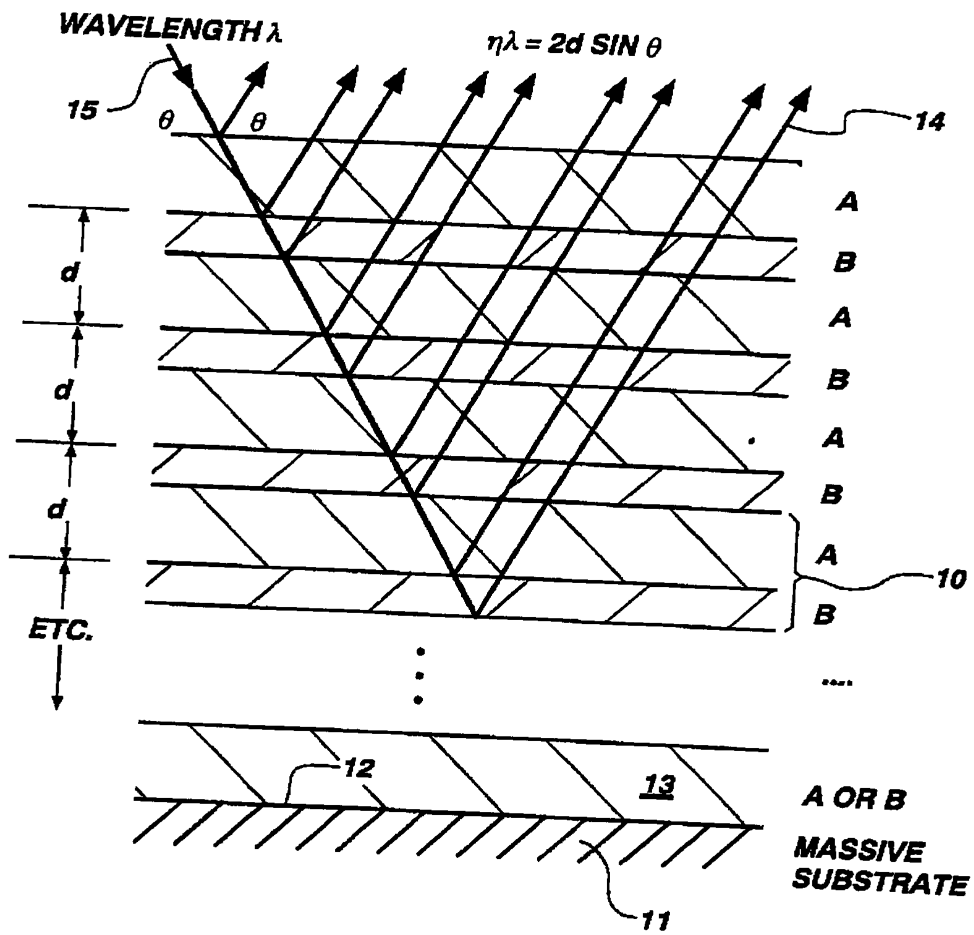
WAVELENGTH λ
ηλ = 2d SIN θ
15
θ
θ
14
A
B
A
B
A
B
A
B
10
d
d
d
ETC.
12
13
A OR B
MASSIVE
SUBSTRATE
11

Fig. 1

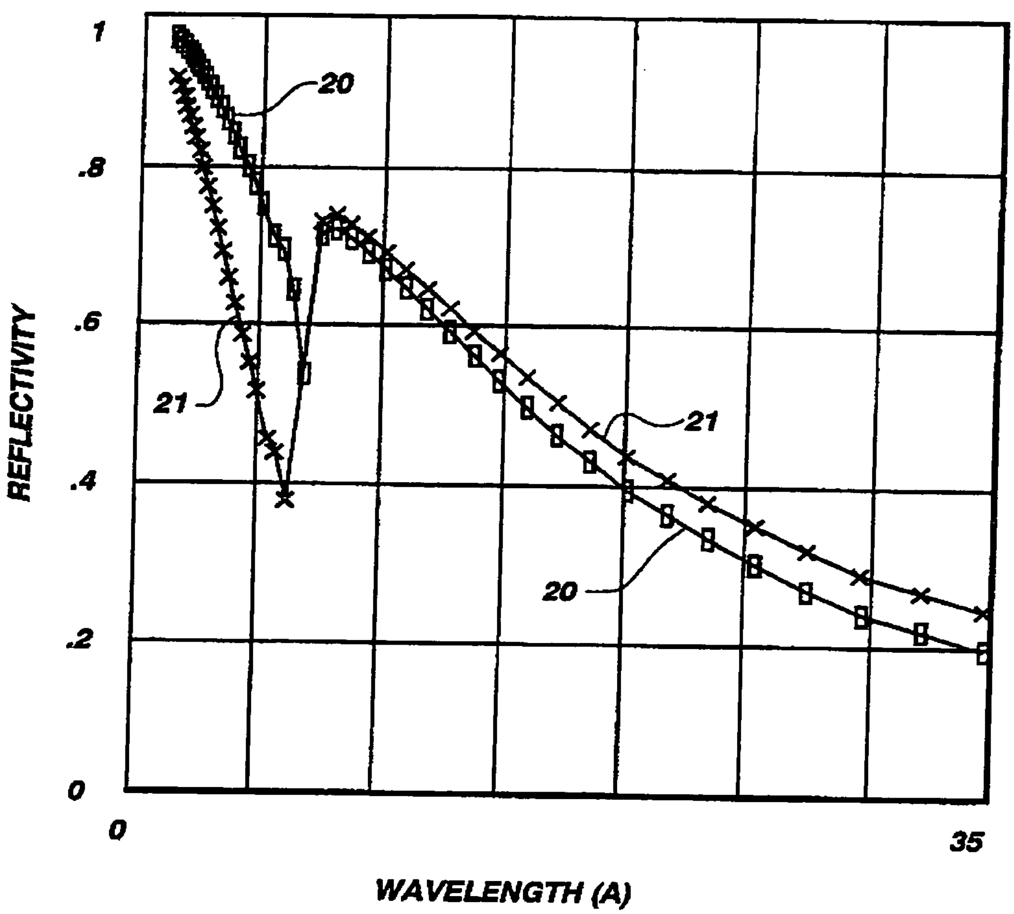

Fig. 2

INTERNATIONAL SEARCH REPORT

PCT/US92/09308

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :G21K 1/06; C23C 14/34

US CL : 204/192.15,192.16,192.26,192.27;378/84,85;428/627,635,660,663,665

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/192.15, 192.16, 192.26, 192.27; 378/84, 85; 428/627, 635, 660, 663, 665

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,727,000 (OVSHINSKY ET AL.) 23 February 1988, see columns 3, 6-9, 11-12 and tables 5a, 7a, 7b, 9a and 10a.	1, 2, 5, 9-16 and 18
X	US, A, 4,675,889 (WOOD ET AL.) 23 June 1987, see column 6, line 20-23.	1, 2, 5, 9-16, and 18
X	US, A, 4,785,470 (WOOD ET AL.) 15 November 1988, see column 5, line 32-35 and column 6, lines 1-35.	1, 2, 5, 9-16 and 18
Y	US, A, 4,663,008 (TAKEOKA ET AL.) 05 May 1987, see column 3 and the examples.	3-4, 6-8 and 17
Y	US, A, 4,992,153 (BERGMANN ET AL.) 12 February 1991, see column 6, lines 15-33.	3-4, 6-8 and 17

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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